



Electric-agitation-enhanced photodegradation of rhodamine B over planar photoelectrocatalytic devices using a TiO₂ nanosized layer

Jing Shang*, Fengwei Zhao, Tong Zhu, Qing Wang, Han Song, Yuchao Zhang

Department of Environmental Sciences, State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, PR China

ARTICLE INFO

Article history:

Received 1 December 2009

Received in revised form 9 February 2010

Accepted 9 February 2010

Available online 16 February 2010

Keywords:

Photoelectrocatalysis

Photocatalysis

ITO/TiO₂/ITO device

TiO₂ film

ABSTRACT

The photocatalytic (PC) and photoelectrocatalytic (PEC) degradations of liquid-phase rhodamine B (RhB) were investigated over titanium dioxide (TiO₂) coated patterned indium tin oxide (ITO) substrate, denoted as planar ITO/TiO₂/ITO device. It is found that over planar ITO/TiO₂/ITO device, the PEC degradation of RhB by a bias of 1.5 V is significantly increased than the PC degradation of RhB, mainly because the horizontal electric field can not only suppress the hole–electron recombination, but also act as an electric agitator to enhance the competitive adsorption of RhB onto the TiO₂ surface. The results show that the planar ITO/TiO₂/ITO device is an alternative way to achieve efficient degradation of dyes with simple configuration.

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1. Introduction

Since textile effluents containing a wide variety of organic dyes discharged from the industries do serious harm to environment and human health, the decomposition or decolorization of dyes is of great importance to the water purification and conservation [1]. In the past decade, tremendous researches have been focused on the photocatalytic oxidation of organic pollutants over titanium dioxide (TiO₂), as it is stable, non-corrosive, environmentally friendly, and cost effective. Nevertheless, the high probability of hole–electron recombination in TiO₂ during the photocatalytic process has to be solved yet [2–4].

Recently, a technique of the photoelectrocatalytic (PEC) removal of dyes in liquid phase was provided [5–8], in which the positive potential applied to TiO₂ coated electrode can force photoelectrons flowing through the TiO₂ film, thereby suppressing the recombination of electrons and holes and promoting the photocatalytic degradation of organic dyes. However, in this system, the photocurrent in TiO₂ is in series connection with Faraday current (electrolyte conduction) and electrochemical current (electro-oxidation and reduction), setting barrier to exactly understanding the major roles the electric field may play in the PEC process. Very recently, a class of planar ITO/TiO₂/ITO device was reported [9], which is able to not only accelerate the photodegradation of gaseous formaldehyde, but also help understand the relevant photophysics process.

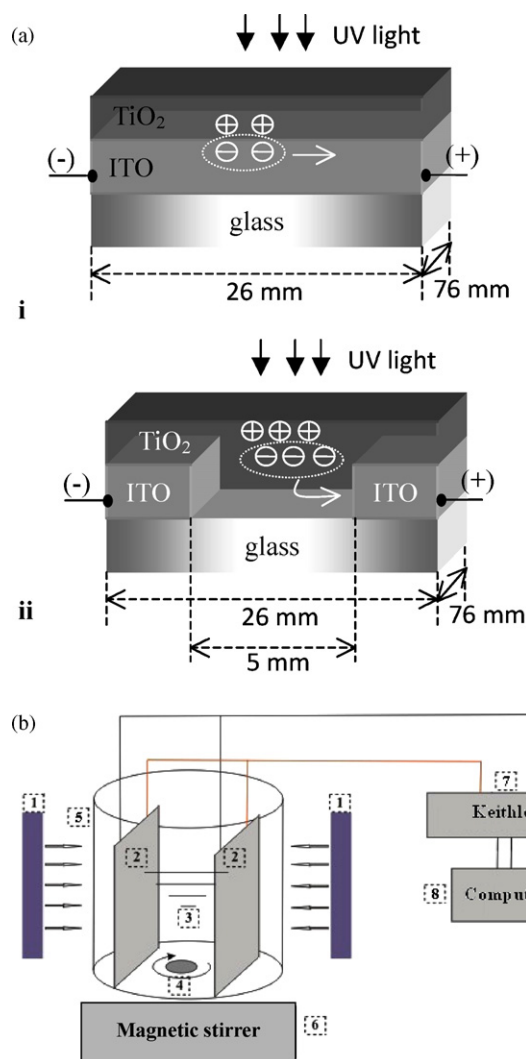
Here, we firstly employ planar ITO/TiO₂/ITO device to the photodegradation of RhB in the liquid phase, and find that the planar device enables the PEC degradation of RhB markedly increased compared to the PC degradation of RhB. The dual effects of the horizontal electric field are also discussed.

2. Experimental

2.1. Preparation and characterization of planar ITO/TiO₂/ITO and TiO₂/ITO device

80 nm thick indium tin oxide (ITO) coated glass substrates (with a resistance of 20 Ω/square) were firstly patterned by hydrogen etching. Then, the patterned ITO substrates were cleaned in an ultrasonic horn consecutively by chloroform, acetone, alcohol, and deionized water [9], and finally dried for 1.0 h at 90 °C. Next, the pre-cleaned, patterned ITO substrate was dipped into a TiO₂ sol (prepared by sol–gel method, with the molar ratio of Ti(OC₄H₉)₄:NH(C₂H₄OH)₂:C₂H₅OH:H₂O being 5:5:133:6) for 2 min and then lifted up at a speed of 2 cm/min. Then, the sample was dried at 90 °C for 10 min and calcined at 480 °C for 1 h. The dip-coating was repeated four times for completing a planar ITO/TiO₂/ITO device. For comparison, TiO₂ thin film was also coated by the same procedure onto non-patterned ITO glass, denoted as planar TiO₂/ITO device. The structures of the two devices are schematically shown in Scheme 1(a). The Raman spectra and morphology observations for the resulting TiO₂ films were conducted on a JY HR800 spectrometer and on an Amray 1910FE scanning electron microscope (SEM), respectively. The film thicknesses were

* Corresponding author. Tel.: +86 10 62756046; fax: +86 10 62756046.
E-mail address: shangjing@pku.edu.cn (J. Shang).



Scheme 1. (a) The structures of planar TiO₂/ITO device (i) and planar ITO/TiO₂/ITO device (ii). Note that, in the planar ITO/TiO₂/ITO device, the dissociation of hole-electron pairs only generated in the TiO₂ area lying between two ITO electrodes is affected by the bias. (b) The geometry of photocatalytic and photoelectrocatalytic reactor: (1) UV lamp; (2) device; (3) rhodamine B solution; (4) magneton; (5) quartz beaker; (6) magnetic stirrer; (7) Keithley 2400 DC sourcemeter; (8) computer.

measured to be about 150 nm using a KLA-Tencor alpha-step IQ surface profiler.

2.2. Apparatus and measurement

The geometry of the photoelectrochemical setup is shown in Scheme 1(b). It is composed of a computer-controlled Keithley 2400 DC sourcemeter, two 8 W bacteria lamp as the UV radiation source (with the main wavelength of 254 nm and the light intensity of 2.3 mW/cm² 7 cm away from the light source by a UV-B photometer), two devices connecting in parallel, a quartz beaker with a height of 10 cm and an inner diameter of 7 cm, a magneton, and a magnetic stirrer. The concentration of RhB in the solution was monitored by measuring the absorbance of sampled solution at 553 nm using Unico 2100 Visible Spectrophotometer. The degradation of RhB over planar device was assumed first-order reaction for the evaluation. The loop current of system was measured using the Keithley 2400 DC sourcemeter.

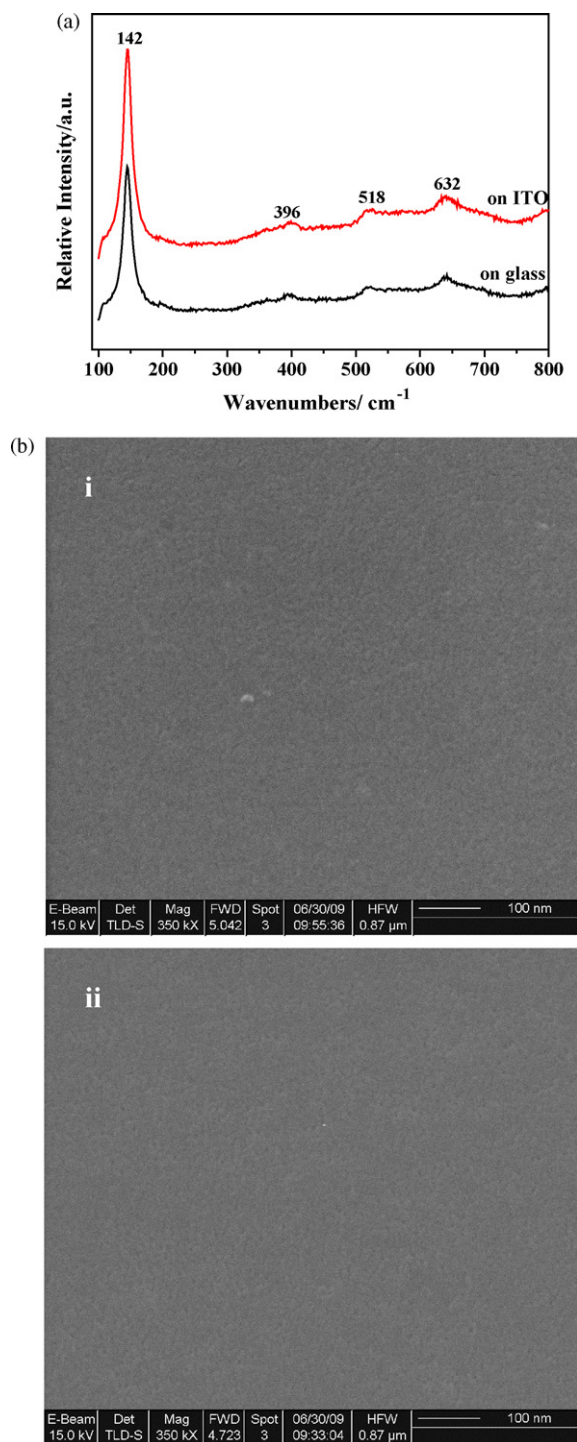


Fig. 1. (a) The Raman spectra of TiO₂ thin films coated on ITO surface and glass surface. (b) The SEM images for TiO₂ thin films coated on ITO (i) and glass (ii) surfaces.

3. Results and discussions

3.1. The morphological characterization of TiO₂ thin films

Fig. 1(a) shows the Raman spectra of TiO₂ thin films coated on ITO surface and glass surface. The characteristic peaks at 142, 396, 518, and 632 cm⁻¹ indicate TiO₂ thin films prepared were mainly anatase structure [10], regardless of the substrate. In addition, Fig. 1(b) shows TiO₂ thin films coated on both ITO surface and

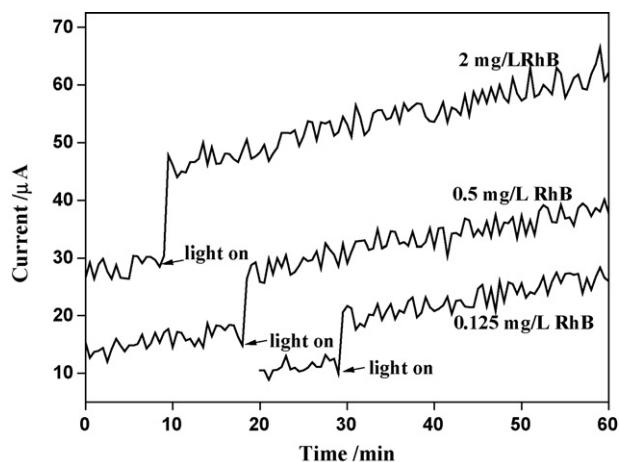


Fig. 2. The plots of the loop current versus time at various initial concentrations of RhB before and after the UV illumination at a bias of 5 V in solution without NaCl.

glass surface were dense and uniform, suggesting that TiO_2 thin film could fully cover patterned ITO glass substrate.

3.2. The functionality comparison between ITO/ TiO_2 /ITO and TiO_2 /ITO devices

The TiO_2 /ITO film has been widely used as a photoanode in the conventional photoelectrocatalytic degradation of organic pollutants. The proposed mechanism for it is that the electric field perpendicular to the TiO_2 film surface will transfer electrons away from their counterparts into the outer circuit, whereby the photocatalytic efficiency is enhanced. However, when the TiO_2 /ITO film is applied as planar device without counter electrode (as shown in Scheme 1(a)(i)), the electric field is confined to near the TiO_2 /ITO interface, leading to the weak coverage of electric field on the planar device surface which is the major place for the photodegradation of dye. Therefore, the planar TiO_2 /ITO device without counter electrode is not suitable to assist the PC degradation of dye by bias and probe the relevant mechanism (see Supplemental information for the details).

While, as seen in Scheme 1(a)(ii), the electric field in the ITO/ TiO_2 /ITO device lies between two ITO electrodes. On the one hand, it is able to effectively enhance the exciton dissociation in the TiO_2 area lying between two ITO electrodes; on the other hand, the electric field can effectively cover the TiO_2 surface between two ITO electrodes, and enable electro-oxidation, Faraday conduction, and electro-reduction therein, creating the electrochemical current in parallel connection with the electronic current of TiO_2 in the reactive system. Hence, the planar ITO/ TiO_2 /ITO device might provide a possibility to deeply investigate the bias influences on the PC degradation of RhB over TiO_2 film in liquid phase. In addition, the compact configuration of planar PEC device, that is, two electrodes lie on a same glass substrate, presents a multi-device connection in parallel without needing counter electrode, greatly simplifying the reactive setup than commonly used PEC methods.

3.3. RhB degradation over planar ITO/ TiO_2 /ITO device

3.3.1. The photocurrent of planar ITO/ TiO_2 /ITO device

Fig. 2 shows the loop currents of aqueous reactive systems using planar ITO/ TiO_2 /ITO device before and after the UV illumination at various initial concentrations of RhB. The dark loop current of system increased from 10 μA at 0.125 mg/L RhB to about 30 μA at 2 mg/L RhB. Because the intrinsic conductivity of TiO_2 (measured in planar ITO/ TiO_2 /ITO device under an inert-gas condition) was in the order of 10^{-7} S/cm, the dark loop current of system mostly resulted

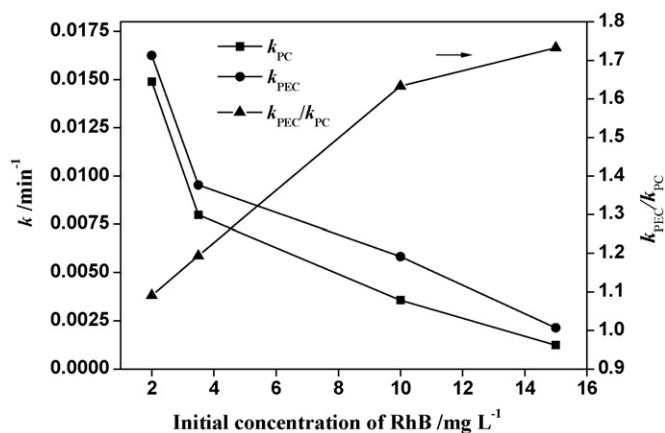


Fig. 3. The plots of k_{PC} (squares), k_{PEC} (circles), and $k_{\text{PEC}}/k_{\text{PC}}$ (uptriangles) versus initial concentration of RhB in solution without NaCl. The planar ITO/ TiO_2 /ITO device was biased at 5 V for the PEC degradation. The electrocatalytic degradation of RhB, as well as photolysis of RhB under the UV illumination, over planar device was found negligible in this case. Note that, if the bias is less than 5 V, the value of $k_{\text{PEC}}/k_{\text{PC}}$ will be small; if the bias is greater than 5 V, the electrocatalytic degradation of RhB will be evident. So the bias of 5 V is optimal to investigate the PEC degradation of RhB over the planar device in solution without NaCl.

from the electrochemical conduction. Upon the illumination, the loop current jumped sharply, reasonably attributed to the photocurrent generation in the system. Furthermore, the amplitude of loop current jump increased with increasing initial concentration of RhB.

The photoinduced electron transfer from TiO_2 to ITO could contribute to the device photocurrent. There are two kinds of TiO_2 /ITO interfaces in the planar ITO/ TiO_2 /ITO device, as shown in Scheme 1(a)(ii). One is the horizontal contact of ITO electrode with TiO_2 . Although electrons can be efficiently generated at the interface, they will not be transferred into the outer circuit, since the electric field only lies between two ITO electrodes. Another is the vertical contact of ITO electrode with TiO_2 . Considering the exciton diffusion length of TiO_2 is in the order of micrometer, the number of excitons dissociated at this interface is concluded negligible. Hence, the two vertical TiO_2 /ITO interfaces act as electrical contacts for the formation of loop current in planar ITO/ TiO_2 /ITO device.

Therefore, it is suggested that the photocurrent consists of two major parts. One is described as follows [2,3]:



Another is the electron transfer from lowest unoccupied molecular orbit (LUMO) of dye to conduction band of photocatalyst, at the condition that LUMO potential of RhB is higher than conduction band of TiO_2 [11]:



Because we did not bubble oxygen gas into the reactive system, the contribution of O_2^- species to the oxidation of RhB was considered minor [12]. Thus, holes existing in the valence band of TiO_2 and other resulting species, such as hydroxyl radical, were considered to answer for the photodegradation of RhB in solution.

3.3.2. Effect of RhB initial concentration on RhB degradation in solution without NaCl

The RhB degradation over planar ITO/ TiO_2 /ITO device in solution containing no NaCl is shown in Fig. 3. The first-order rate constant of the reaction without bias and with the illumination (k_{PC}) decreased from 0.015 min^{-1} at 2 mg/L RhB to 0.0012 min^{-1} at 15 mg/L RhB,

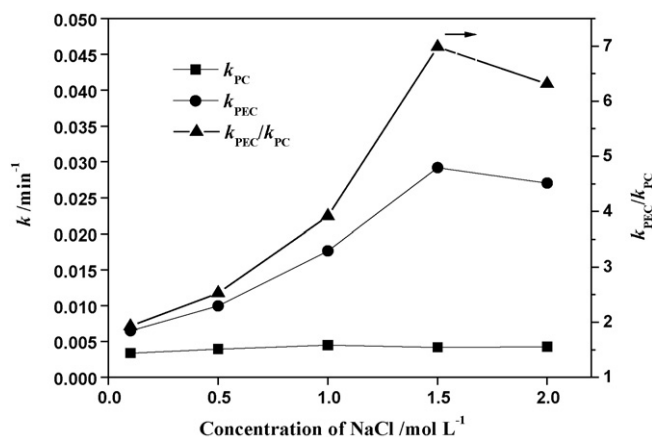


Fig. 4. Effects of NaCl concentration on the PC and PEC degradations of RhB over planar ITO/TiO₂/ITO device with an initial RhB concentration of 10 mg/L and a bias of 1.5 V. The electrocatalytic degradation of RhB, as well as photolysis of RhB under the UV illumination, was found negligible in this case.

while the first-order rate constant of the reaction with a bias of 5 V and with the illumination (k_{PEC}) decreased from 0.016 min⁻¹ at 2 mg/L RhB to 0.0021 min⁻¹ at 15 mg/L RhB. It is also seen that the value of k_{PEC}/k_{PC} increased dramatically with increasing initial concentration of RhB, demonstrating the synergistic effect of bias on the photocatalytic degradation of RhB (SEBD) is subject to initial concentration of RhB.

It is widely accepted that the bias can improve the dissociation efficiency of hole-electron pairs in TiO₂, thereby facilitating the PC degradation of dye in liquid phase. However, the strong dependence of k_{PEC}/k_{PC} value on initial concentration of RhB suggests that the bias should play an extra, important role in the planar device. Here, we consider the bias (the horizontal electric field) may act as an electric agitator to accelerate the competitive adsorption of RhB onto the surface of TiO₂ film, giving rise to the enhanced PC degradation of RhB. The RhB molecules are adsorbed onto the TiO₂ surface and subsequently photooxidized into intermediates [13,14]. If the resulting intermediates bonded to TiO₂ surface cannot be removed immediately, the following RhB molecules will be delayed from being adsorbed onto TiO₂, thereby decelerating the photocatalytic reaction. Under the condition without bias, these intermediates may be pulled from TiO₂ due to the collisions by water molecules. Under the condition with bias, there co-exists an additional process that the horizontal electric field pulls those intermediates away from TiO₂ surface, which is considered as the extra, important effect of bias on the PC degradation of RhB over planar device. When initial concentration of RhB is low, the competitive adsorption of RhB molecules onto TiO₂ is not severely blocked by the resulting intermediates, so the SEBD is weak, for example, k_{PEC}/k_{PC} was only 1.09 at 2 mg/L RhB. When initial concentration of RhB is high, the competitive adsorption of RhB molecules onto TiO₂ is severely blocked by the charged intermediates, so the SEBD is remarkable, for example, k_{PEC}/k_{PC} increased to 1.73 at 15 mg/L RhB.

3.3.3. Effect of NaCl concentration on RhB degradation

Fig. 4 shows the influences of NaCl concentration on the degradation of RhB over planar device. The k_{PC} was slightly dependent on NaCl concentration, implying that there was no obvious competitive adsorption between NaCl and RhB onto TiO₂ film. It is likely because NaCl could dissolve in water completely and would not occupy the active sites on the TiO₂ surface [15]. However, the photodegradation of RhB over planar device was greatly improved by bias. The k_{PEC} increased from 0.0065 min⁻¹ at 0.1 mol/L NaCl to 0.029 min⁻¹ at 1.5 mol/L NaCl, and then decreased to 0.027 min⁻¹

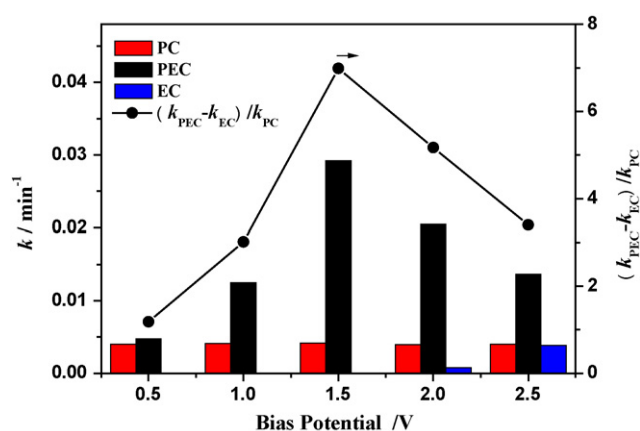


Fig. 5. Effect of anode bias on the degradations of RhB over planar ITO/TiO₂/ITO device with an initial RhB concentration of 10 mg/L in 1.5 mol/L NaCl solution.

at 2 mol/L NaCl. The k_{PEC}/k_{PC} showed the similar variation with NaCl concentration as k_{PEC} , and achieved a maximum value of 7 at 1.5 mol/L NaCl. The much increased PEC degradation of RhB in solution with NaCl than in solution without NaCl could be interpreted as follows. On the one hand, the Cl⁻ ions adsorbed on TiO₂ surface were oxidized to Cl[•] by holes and hydroxyl radicals according to the following reactions [16,17]:



Cl[•] could be further converted to other active chlorine species such as Cl₂, HClO, and ClO⁻, which are much more oxidative than photo-generated holes and hydroxyl radicals [17,18]. On the other hand, the movement of hydrated Na⁺ along TiO₂ film is considered greatly enhanced by the bias, i.e. the electric agitation, and correspondingly the collisions of these hydrated ions to the intermediates bonded to TiO₂ is enhanced; thus, these intermediates are quickly pulled away from TiO₂ surface and the following RhB molecules can be efficiently adsorbed onto TiO₂ surface, therefore greatly promoting the whole photodegradation process in combination with the oxidation of Cl⁻ into Cl. Nevertheless, when NaCl concentration is too high, though the generation of active chlorine species is efficient, the adsorption of RhB onto TiO₂ film has to be reduced due to the too strong collisions by hydrated ions, resulting in the saturation of k_{PEC} as shown in Fig. 4.

3.3.4. Effect of electrode potential on RhB degradation

The electrode potential is an important parameter to influence the PEC degradation of RhB. On the one hand, the electrode potential can tilt the conduction band of TiO₂ thin film and transport electrons into outer circuit; on the other hand, it also affects the electrochemical reactions and the adsorption and desorption of RhB on the device surface. As seen in Fig. 5, at a bias ≥ 2 V, the electrocatalytic degradation of RhB became obvious. The value of $(k_{PEC} - k_{EC})/k_{PC}$ increased with the bias ranging from 0.5 V to 1.5 V, and then decreased with the bias increasing from 1.5 V to 2.5 V. It demonstrates that if the bias is too high, the horizontal electric field will drive hydrated ions to pull the RhB molecules away from TiO₂ surface so overmuch that the SEBD is reduced accordingly.

3.3.5. The PEC stability of planar ITO/TiO2/ITO device

To evaluate the stability of ITO/TiO₂/ITO device, the PEC RhB degradation was repeatedly performed over a same ITO/TiO₂/ITO device, as depicted in Fig. 6. The degradation rate remained virtually unchanged during the ten experiments. This indicates the good

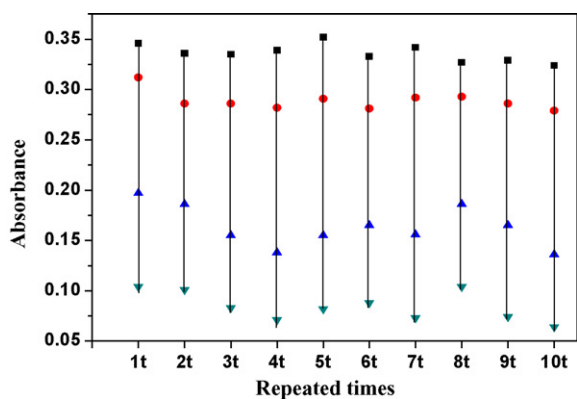


Fig. 6. Ten continuous PEC degradations of RhB over a same ITO/TiO₂/ITO device with RhB initial concentration of 1.5 mg/L and a bias of 1.5 V in 1.0 mol/L NaCl solution. Each PEC degradation was carried out for 5 min.

adhesion of TiO₂ film to the ITO substrate and the stable activity of planar device in the PEC degradation of RhB. Therefore, the planar ITO/TiO₂/ITO device is a promising alternative to the conventional, two-electrode PEC method.

4. Conclusions

The effects of RhB initial concentration, NaCl concentration, and bias on the degradations of RhB over planar ITO/TiO₂/ITO device have been investigated. It is found that in the planar device, besides reducing the hole–electron recombination, the horizontal electric field plays an extra role of an electric agitator to alter the competitive adsorption onto TiO₂ film. The rate constant ratio of PEC to PC for RhB is 7 over the planar device under the condition that the bias is 1.5 V, the initial concentration of RhB is 10 mg/L, and the concentration of NaCl is 1.5 mol/L.

Acknowledgements

The authors are grateful to the financial support by the National Natural Science Foundation of China (20407002), the Special Funds for Major State Basic Research Projects (2002CB410802) and the Special Funds for State Key Joint Laboratory of Environmental Simulation and Pollution Control (2008).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.apcatb.2010.02.018](https://doi.org/10.1016/j.apcatb.2010.02.018).

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